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Quantum chemical analysis of carbon dioxide absorption into aqueous solutions of moderately hindered amines

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Abstract

Aqueous solutions of moderately hindered amines are promising absorbents for the capture of CO_2 from a gas stream because of their relatively low heats of reaction and high rates of absorption. To determine the reaction mechanisms underlying the absorption process, we performed a quantum chemical analysis of the absorption of CO_2 into aqueous amine solutions and carried out an experimental comparison of representative amines. We correlated properties such as absorption capacity and product ratio with results from free energy calculations using the conductor-like screening model for real solvents (COSMO-RS) coupled with density functional theory (DFT). Additionally, the reaction mechanisms were investigated by transition state optimizations and intrinsic reaction coordinate (IRC) calculations in an aqueous solution phase by DFT calculations using the latest continuum solvation model (SMD/IEF-PCM). The results indicated that a bicarbonate anion likely forms directly by the reaction of CO_2, H_2O and an amine rather than by the hydrolysis of a carbamate anion.

Keywords: amine absorbent; sterically hindered amine; quantum chemistry; solvation model; activation energy

1. Introduction

Aqueous solutions of sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) and 2-piperidineethanol (2-PE) have attracted attention as attractive absorbents for the capture of CO_2 from a gas stream [1-3]. The advantages of these sterically hindered amines include a large capacity for CO_2 absorption with relatively low heat of reaction and a high rate of absorption, which leads to a lower regeneration energy and a higher recovery capacity. For the efficient use of these amines and the development of novel absorbents, it is important to understand the mechanisms of CO_2 absorption by the aqueous solutions of sterically hindered amines based on their molecular structures.

In aqueous amine solutions, CO_2 is absorbed by the formation of carbamate or bicarbonate anions as follows:

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$$2B + CO_2 \leftrightarrow B'COO^- + BH^+ \quad (1)$$

$$B + CO_2 + H_2O \leftrightarrow HCO_3^- + BH^+ \quad (2)$$

where B denotes an amine and B′ implies the deprotonation of the amino group. Generally, both reactions could proceed in aqueous solutions of primary or secondary amines. Therefore, the product ratio between the carbamate anion and the bicarbonate anion is one of the most important factors in the performance of the absorbent.

For sterically hindered amines, carbamate is not stable because of steric hindrance by the substituents adjacent to the amino group and, therefore, the product ratio of carbamate to bicarbonate is low. This fact is widely known and has been shown experimentally [2-4]. However, the relationships between the extent of steric hindrance and the absorbent's properties are not clear. Previous studies have shown that the reactivity of the amino group is governed by steric hindrance and other factors such as molecular orbitals, hydrogen bonding and solvation [4,5]. In this work, we quantitatively evaluate the reactivity of the amino group by a quantum chemical approach and compare the calculation results with experimental data.

As mentioned above, the bicarbonate anion is the main product of the CO_2 absorption reaction in aqueous solutions of sterically hindered amines. Apart from reaction (2), a plausible reaction pathway for the formation of the bicarbonate anion is the hydrolysis of a carbamate anion.

$$B'COO^- + H_2O \leftrightarrow HCO_3^- + B \quad (3)$$

To determine possible reaction pathways, including transition states, we performed intrinsic reaction coordinate (IRC) calculations in an aqueous solution phase by density functional theory (DFT) with the latest continuum solvation model [6]. The IRC calculations were carried out for reactions (1)-(3) of 2-isopropylaminoethanol (IPAE), which is a moderately hindered amine with high performance as will be shown later. The IRC calculations resulted in a comprehensive understanding of the CO_2 absorption mechanism.

Table 1. Tested amines and results summary.
pK_a data at room temperature from references [a] [4], [b] [11] and [c] [12]. [d] maximum loading of CO_2 (mol CO_2/mol amine) in Figure 2. [e] difference between the reaction free energies of carbamate and bicarbonate anion formation, $\Delta G_{(1)} - \Delta G_{(2)}$ at 25 °C calculated by COSMO-RS//BP/TZVP (kcal/mol). [f] steric hindrance of the amino group.

amine		pK_a	max loading [d]	$\Delta\Delta G$ [e]	hindrance [f]
monoethanolamine	MEA	9.53 [a]	0.53	–4.2	mild
2-(butylamino)ethanol	nBAE	9.92 [a]	0.66	–2.6	
2-(isopropylamino)ethanol	IPAE	9.93 [a]	0.78	–1.7	moderate
2-amino-2-methyl-1-propanol	AMP	9.69 [b]	0.74	–1.5	
2-piperidineethanol	2-PE	10.14 [b]	0.87	0.3	
2-(tert-butylamino)ethanol	tBAE	10.29 [c]	0.84	5.5	severe

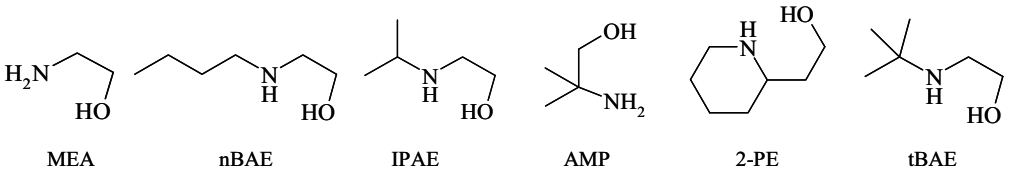

Figure 1. Molecular structures of the investigated amines.

2. Methods

To evaluate the reactivity of the amine in reactions (1) and (2) we obtained the Gibbs free energies of the reactions by calculating the free energy of each species in an aqueous solution using the conductor-like screening model for real solvents (COSMO-RS) coupled with DFT [4,7]. Geometry optimizations for each species in the COSMO model were carried out at the BP/TZVP level using the resolution of identity (RI) approximation [8]. For the DFT calculations, the most stable conformation in vacuum as determined using molecular mechanics with the MMFF force field [9] was set as the initial geometry. The programs COSMO*therm* (Ver. 3.2), TURBOMOLE (Ver. 1.0) and Spartan (′06) were used for the above-mentioned calculations.

DFT calculations with the SMD solvation model using the integral-equation-formalism polarizable continuum model (IEF-PCM) protocol for bulk electrostatics were carried out for transition state optimizations and subsequent IRC analyses at the B3LYP/6-31G(d) level [6]. The geometries of the resulting reactants and products were optimized at the same level followed by IRC calculations. Using these calculated energies, the activation energy of a reaction was evaluated by $E_{TS} - E_R$ and that of the inverse reaction was evaluated by $E_{TS} - E_P$ where E_{TS}, E_R and E_P are the total energies of the transition state, the reactants and the products, respectively. Vibration frequencies were also calculated to confirm that the obtained geometries were stable or transition structures. The Gaussian09 program [10] was used for the calculations at the SMD/IEF-PCM/B3LYP/6-31G(d) level.

For an experimental comparison of the representative amines, we used a gas composition of 20 % CO_2 with the balance being N_2 and let it flow at a rate of 700 ml/min into 50 ml of a 30 wt% aqueous amine solution. A glass scrubbing bottle was used as the vessel in a water bath controlled at 40 °C for 60 min and then the bottle was moved to another water bath that was controlled at 70 °C. The outlet gas was monitored with a carbon dioxide analyzer (VA-3001, Horiba) to measure the CO_2 loading in the solution. For nuclear magnetic resonance (NMR) analysis, CO_2 loaded aqueous amine solutions were prepared at 40 °C for less than 60 min and 100 μL of D_2O was added to 500 μL of each solution. ^{13}C-NMR spectra were recorded at 100 MHz and at room temperature (JNM-ECA400, JEOL). To obtain quantitative spectra, the inverse-gated decoupling technique was used with a delay of 30 s, a pulse width of 9 μs and 400 scans. Amines with 97–99 % purity were purchased from various chemical companies and used without further purification.

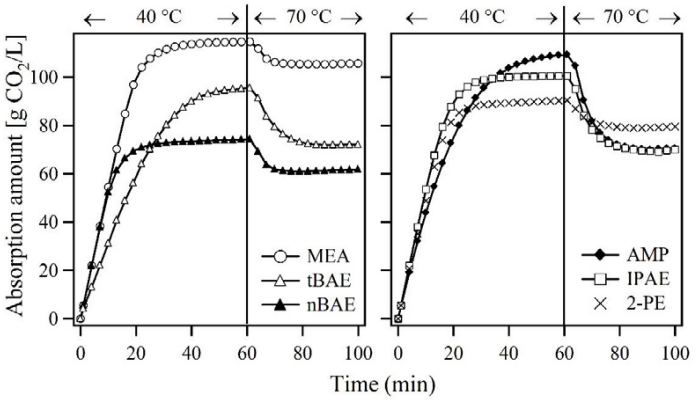

Figure 2. CO_2 absorption and desorption of the 30 wt% aqueous amine solutions.

3. Results and Discussion

The difference between the Gibbs free energies of reactions (1) and (2), $\Delta G_{(1)} - \Delta G_{(2)}$ ($\equiv \Delta\Delta G$), is directly related to the stability of the carbamate. The calculated values of $\Delta\Delta G$ for the representative amines are summarized in Table 1. The molecular structures of the amines are shown in Figure 1. Results of an experimental comparison between the amines are shown in Figure 2. The maximum loadings that are defined by molar ratios of absorbed CO_2

to total amine at 60 min in the present experiments, and pK_a values for the amines are listed in Table 1.

$$pK_a = -\log_{10}([B][H_3O^+]/[BH^+]) \quad (4)$$

The pK_a values in Table 1 are all within the same range. $\Delta\Delta G$ can, therefore, be used without correction to measure the product ratio of carbamate to bicarbonate [4].

The calculated $\Delta\Delta G$ values for monoethanolamine (MEA) and 2-(butylamino)ethanol (nBAE) are −4.2 kcal/mol and −2.6 kcal/mol, respectively, while that for 2-(tert-butylamino)ethanol (tBAE) is 5.5 kcal/mol. These results indicate that CO_2 is mainly absorbed by the formation of carbamate anion in aqueous solutions of mildly hindered amines such as MEA and nBAE. On the other hand, because of the steric effect of the bulky tertiary butyl group, virtually no carbamate forms in aqueous tBAE solutions and only bicarbonate formation occurs. Consequently, MEA and nBAE both have lower loadings and higher absorption rates while tBAE has a higher loading and a lower absorption rate, as shown in Table 1 and Figure 2.

The calculated values of $\Delta\Delta G$ for IPAE, AMP and 2-PE are moderate at −1.7 kcal/mol, −1.5 kcal/mol and 0.3 kcal/mol, respectively. This indicates that for these amines the product ratio of carbamate to bicarbonate anion is low compared with MEA or nBAE. The CO_2 absorption rates, loadings and desorption efficiencies of these moderately hindered amines are sufficiently high as shown in Figure 2. Among them aqueous IPAE solutions absorb CO_2 at a relatively high rate and desorb CO_2 with high efficiency.

Figure 3 shows the product ratios of carbamate to bicarbonate anion measured by ^{13}C-NMR. In MEA, the carbamate product dominates the bicarbonate product and this is in agreement with the calculation results. On the other hand, in AMP and IPAE, the bicarbonate anion is the main product. It should be noted that a small but significant amount of carbamate has been observed in these moderately hindered amines, which probably explains the properties of these amines such as their high rates.

The IRC analysis that was used to investigate the reaction pathways including transition states is more informative in determining detailed reaction mechanisms. For the reactions of IPAE, transition states optimized at the SMD/IEF-PCM/B3LYP/6-31G(d) level are shown and denoted as TS1-TS3 in Figures 4-6 where the IRC calculation results are also shown. The calculated activation energies are summarized in Table 2. In reality, a number of conformational geometries should be considered for the reaction pathways. We confirmed that the CO_2 absorption mechanism supported by this work is hardly affected by the conformational effect.

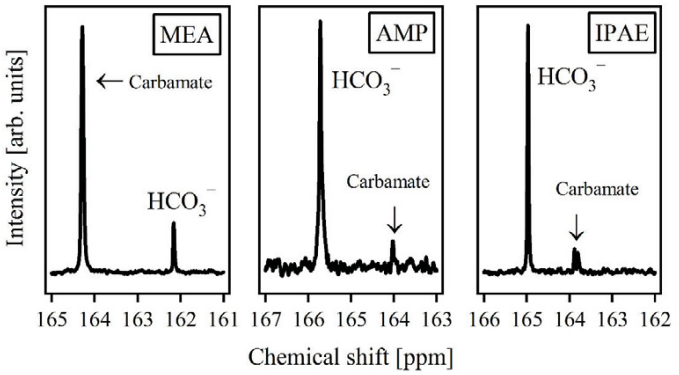

Figure 3. ^{13}C-NMR spectra of the CO_2 loaded aqueous amine solutions. The loadings (mol CO_2/mol amine) are 0.5, 0.3 and 0.4 for MEA, AMP and IPAE, respectively.

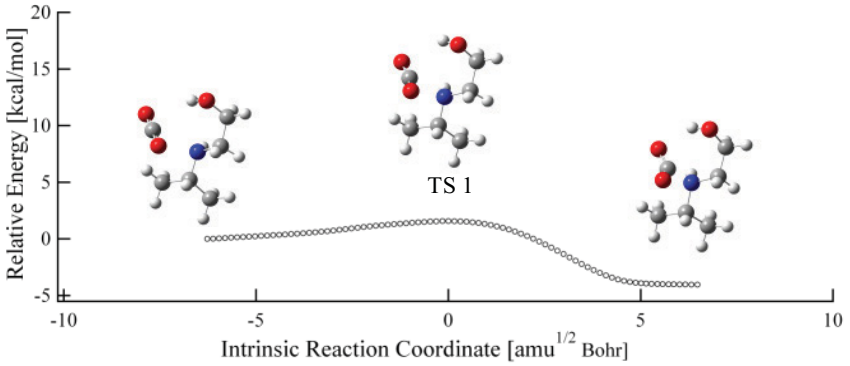

Figure 4. Energy profile along the IRC for the transition state (TS1) in IPAE + CO_2 → IPAE$^+$COO$^-$. The resulting reactants and products are also shown. Calculations were carried out at the SMD/IEF-PCM/B3LYP/6-31G(d) level.

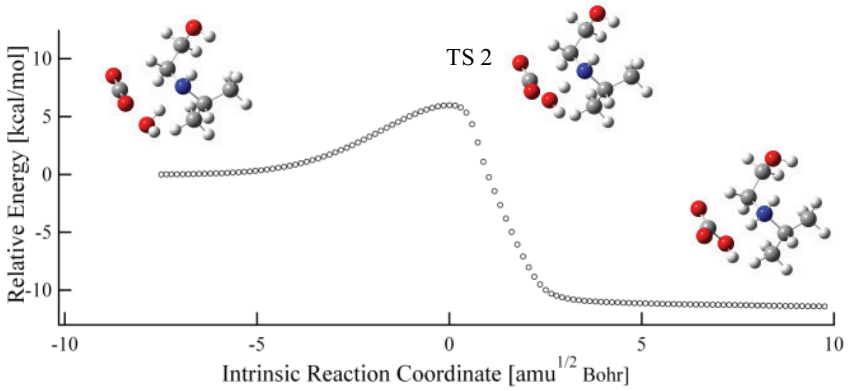

Figure 5. Energy profile along the IRC for the transition state (TS2) in IPAE + H_2O + CO_2 → HCO_3^- + H$^+$IPAE. The resulting reactants and products are also shown. Calculations were carried out at the SMD/IEF-PCM/B3LYP/6-31G(d) level.

As for reaction (1), it has been controversial whether the reaction occurs in a single step or proceeds by the formation of a zwitterionic intermediate. An IRC calculation has confirmed that the zwitterion forms in water as shown in Figure 4.

$$\text{IPAE} + CO_2 \leftrightarrow \text{IPAE}^+\text{COO}^- \tag{5}$$

In aqueous amine solutions, the formed zwitterion is easily deprotonated to form a carbamate anion by reaction with a base.

$$\text{IPAE}^+\text{COO}^- + \text{IPAE} \leftrightarrow \text{IPAE}'\text{COO}^- + \text{H}^+\text{IPAE} \tag{6}$$

However, because of steric hindrance, the carbamate product is not stable. Therefore, by the reverse reactions of (5) zwitterion formation and (6) the deportation of the zwitterion, carbamate would decompose into the reactants of reaction (5).

As shown above, the main product of CO_2 absorption in aqueous IPAE solutions is the bicarbonate anion. Possible reaction pathways to yield bicarbonate product are shown as reactions (2) and (3). The IRC calculation results for these reactions are shown in Figures 5 and 6. The calculated activation energies for the reactions in Figures 5 and 6 are 6.0 kcal/mol and 42.5 kcal/mol, respectively, as listed in Table 2. The difference between these

calculated values is significant even allowing for the possible involvement of additional molecules or other conformations. Considering the high activation energy of reaction (3) it seems that the bicarbonate anion is not formed by the hydrolysis of the carbamate anion.

The calculated activation energies for the inverse reactions are also summarized in Table 2. The energy barrier for the inverse reaction of zwitterion formation is not too high (5.6 kcal/mol) and is comparable to that for bicarbonate anion formation (6.0 kcal/mol). Additionally, for the inverse reaction of bicarbonate anion formation, the energy barrier is as high as 17.7 kcal/mol because of product stability. Thus, these calculation results agree with our experiments because bicarbonate was found to be the main product in the IPAE–H_2O–CO_2 system and indicate that the carbamate anion formed under non-equilibrium conditions is likely to degrade by the reverse reactions.

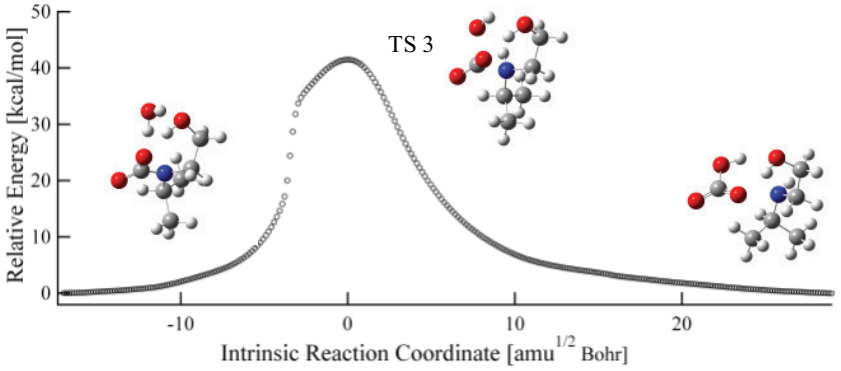

Figure 6. Energy profile along the IRC for the transition state (TS3) in IPAE′COO + H_2O → HCO_3^- + IPAE where IPAE′ implies the deprotonation of the amino group. The resulting reactants and products are also shown. Calculations were carried out at the SMD/IEF-PCM/B3LYP/6-31G(d) level.

Table 2. Calculated activation energies for the IPAE–H_2O–CO_2 reactions.
[a] Transition states shown in Figures 4-6. [b] IPAE′ implies the deprotonation of the amino group.
[c] values calculated at the SMD/IEF-PCM/B3LYP/6-31G(d) level for the forward and inverse reactions (kcal/mol).

TS [a]	reactants [b]	products	activation energies [c]	
			forward	inverse
1	IPAE, CO_2	IPAE$^+$COO$^-$	2.7	5.6
2	IPAE, CO_2, H_2O	HCO_3^-, H^+IPAE	6.0	17.7
3	IPAE′COO$^-$, H_2O	HCO_3^-, IPAE	42.5	42.8

4. Conclusions

Aqueous solutions of moderately hindered amines such as 2-isopropylaminoethanol (IPAE) showed favorable properties for CO_2 absorption: a high absorption rate and a large capacity. We calculated the free energies of CO_2 absorption reactions using the conductor-like screening model for real solvents (COSMO-RS) coupled with density functional theory (DFT). The calculations gave satisfactory amine molecular properties including the effect of steric hindrance for the substituents adjacent to the amino group and the results agreed well with the experimental results. Small but significant amounts of carbamate were detected in the CO_2 loaded aqueous solutions of the moderately hindered amines.

Using the latest continuum solvation model (SMD/IEF-PCM), intrinsic reaction coordinate (IRC) calculations in the aqueous solution phase were also performed by DFT calculations for reactions in the IPAE–H_2O–CO_2 system.

The calculated activation energies were compared and we conclude that carbamate forms easily and decomposes reversibly. Bicarbonate forms directly from IPAE, H_2O and CO_2, and the carbamate hardly undergoes hydrolysis. In aqueous solutions of the moderately hindered amines, carbamate formation seems to play a key role in CO_2 absorption, even though the carbamate anion is a minor product.

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